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CITATION:

Koizumi, Naokazu ...[et al]. Dielectric Relaxation in Gamma-Irradiated Tetrafluoroethylene-Hexafluoropropylene Copolymers at Low Temperatures (Special Issue on Physical, Chemical and Biological Effects of Gamma Radiation, IX). Bulletin of the Institute for Chemical Research, Kyoto University 1968, 46(1): 30-36

ISSUE DATE:

1968-03-30

URL:

http://hdl.handle.net/2433/76224

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 46, No. 1, March 1968

Dielectric Relaxation in Gamma-Irradiated Tetrafluoroethylene-Hexafluoropropylene Copolymers at Low Temperatures

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Received January 24, 1968

Dielectric properties of copolymers of polytetrafluoroethylene and hexafluoropropylene were studied over the temperature range of 78 to 300°K at frequencies of 10 Hz to 100 kHz. Two relaxation regions were observed for both unirradiated and irradiated copolymers : one (the γ relaxation) appeared near 250°K and the other (the δ relaxation) at about 120°K at 100 kHz, respectively. The size of the γ loss peak increased with increasing the irradiation dose and decreased with the degree of crystallinity. The size of the δ loss peak, being much smaller than that of the γ one, increased not only with the irradiation dose but also with the heat treatment for annealing. The activation enthalpy and entropy were 16 kcal./mole and 30 eu for the γ relaxation and 3.5 kcal./mole and 0 eu for the δ relaxation, respectively. The values of these activation parameters in the γ relaxation increased slightly with increased irradiation doses, but those for the δ relaxation was not much influenced with the irradiation. The δ relaxation would be attributed to the dielectric relaxation of end groups in the copolymer. Infrared absorption spectra of highly irradiated copolymers showed the presence of the carboxylic group.

INTRODUCTION

It has been reported that copolymers of tetrafluoroethylene and hexafluoropropylene (TFE-HFP copolymer) exhibit the α and γ dielectric relaxations[1] in accordance with the mechanical behavior[2,3] between 230 and 450°K and that the α relaxation arises from the molecular motion of the main chain in the copolymer ; the γ one is due to the motion of short segments at or near the end of the molecular chain. These arguments were supported by the results on dielectric measurements of γ-irradiated TFE-HFP copolymers[4].

Although Eby and Wilson did not observed the α relaxation in their dielectric measurements, they found another small peak of the dissipation factor at lower temperatures in this copolymer and suggested that the end CF_2H group would be responsible for this lower-temperature relaxation[3]. The present work was undertaken to elucidate the mechanism of such a dielectric relaxation at low temperature as to be associated with the end groups. In this connection it was necessary to make precision measurements of dielectric properties at low temperature in this copolymer and also to investigate the effects of γ-irradiation on the relaxation, since the irradiation causes the scission of the molecular chain and would produce some polar groups at the end of molecular chain.

This paper reports the dielectric relaxation of THF-HFP copolymers in the

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low-temperature region and the effects of γ-irradiation on the relaxation. Also some discussions are presented about the relation between the dielectric properties and the infrared spectra of irradiated copolymers.

EXPERIMENTAL

TFE-HFP copolymer samples used were Teflon 100 from E. I. du Pont de Nemours and Company, Inc. The HFP content in the copolymer was about 11.9 mole% as determined with the infrared method[5]. Specimens for dielectric measurements were thin films of 50 mm in diameter and 0.14 mm thick. The γ-irradiation was carried out in air by utilizing the 2 kCi ^{60}Co gamma-ray irradiation facility at this institute. Some of samples were annealed for 16 hr. at 200°C after irradiation to vary the degree of crystallinity. The degree of crystallinity was determined by the X-ray diffraction method. The density at 25°C was measured with the buoyancy method using *n*-butanol. Infrared spectra in the 3700 $\sim$1650 cm^{-1} region were taken of the same specimen as used for dielectric measurements to detect the formation of a polar group such as the CO group. Physical properties of the samples studied are tabulated in Table 1. Measurements of capacitance and conductance were made with a transformer bridge at frequencies of 10 Hz to 100 kHz in the same way as reported previously[1]. Dielectric measurements in a temperature range from 300 to 78°K were carried out with a newly constructed cell.

Table 1. Physical properties of the samples.

Sample no.	Total irradiation dose, MR	Annealing	Crystallinity, %	Density, g/ml at 25°C
1	0	no	35	2.132
2	0	yes	41	2.152
3	1	no	41	2.136
4	1	yes	45	2.151
5	3	no	38	2.132
6	3	yes	49	2.157
7	10	no	40	2.136

RESULTS

Almost no dependence of the dielectric constant ε' was found on frequency for all the sample studied. The dielectric constant decreased almost linearly with increasing temperature and there was a change near 160°K in the slope of the curve of ε' versus temperature. The γ and δ loss peaks took place above and below about 160°K, respectively. Typical examples of plots of the dielectric loss ε'' versus temperature (t in °C and T in °K) are shown for samples 2 and 5 in Figs. 1 and 2, respectively. The size of the δ loss peak was much smaller than that of the γ loss one. Variation of these loss peaks with irradiation and heat treatment are illustrated for the curves of ε'' versus temperature at 100 kHz in Fig. 3. The temperatures at which two relaxations occurred depended

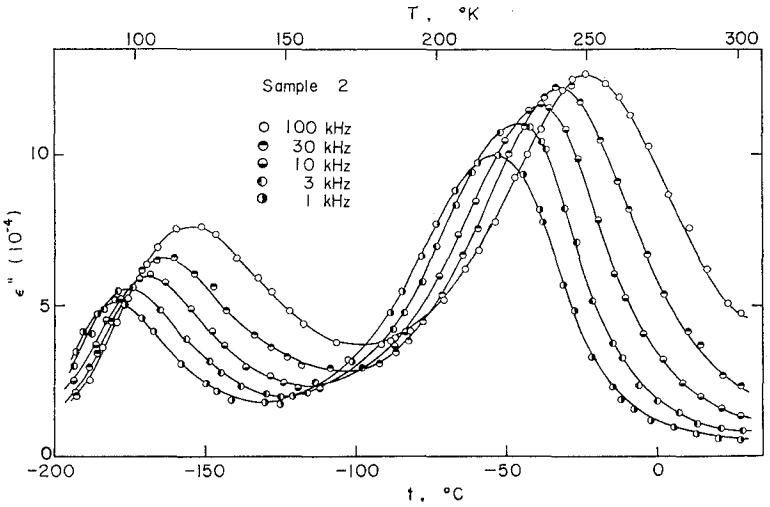

Fig. 1. Dielectric loss ε'' versus temperature for sample 2 at different frequencies.

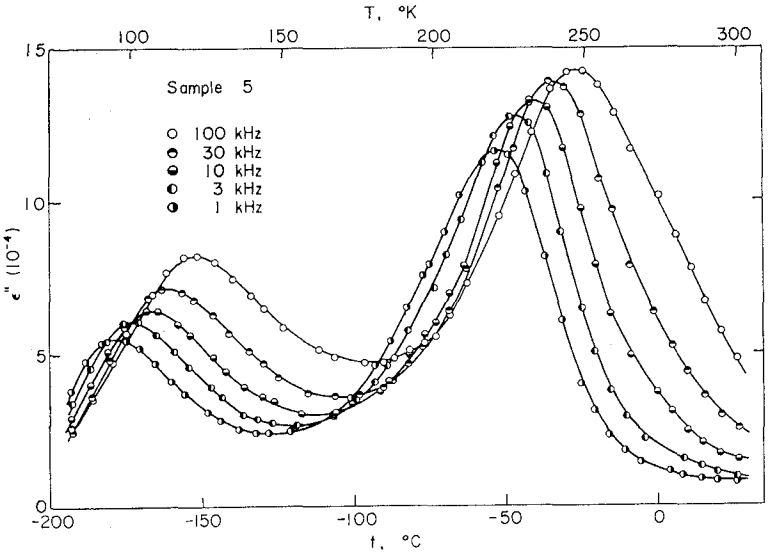

Fig. 2. Dielectric loss ε'' versus temperature for sample 5 at different frequencies.

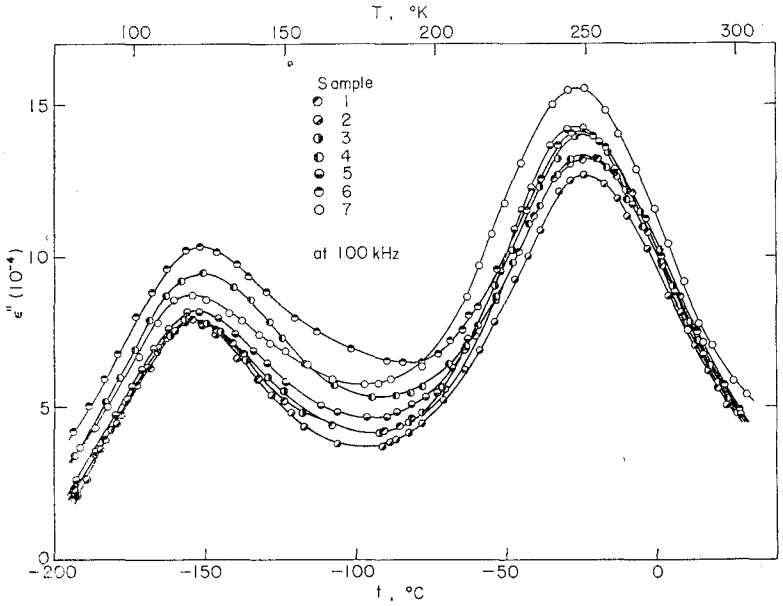

Fig. 3. Dielectric loss ε'' versus temperature at 100 kHz for samples with different irradiation doses.

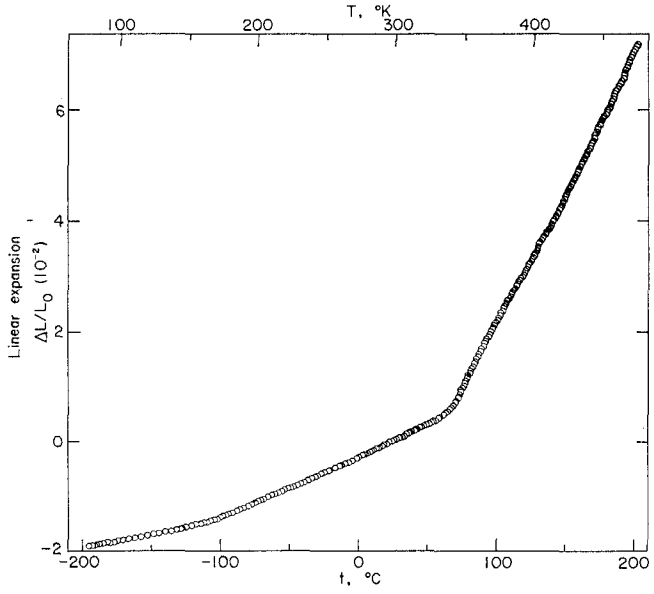

Fig. 4. Linear expansion of TFE-HFP copolymer between −196 and +200°C.

on neither the irradiation dose nor the degree of crystallinity. The linear expansion data taken with a rod sample of Teflon 100 exhibited another transition a 163°K[6] in addition to the one at 333°K[1,4], as seen from Fig. 4.

DISCUSSION

It is an interesting feature that the γ and δ relaxations appeared above and below a transition temperature near 160°K which was found with the linear expansion measurement (Figs. 1, 2 and 4). To examine the effects of γ-irradiation on the γ and δ relaxations the values of loss maxima at 100 kHz are listed in Table 2. With the γ relaxation the magnitude of loss peak increased with increasing the irradiation dose, but decreased with increased degree of crystallinity by annealing. Hence, it is evident that γ-irradiation caused the chain scission and increased the number of short segements responsible for the relaxation and that an increase in crystallinity hindered the polirization associated with the γ relaxation, as was discussed in the previous papers[1,4]. The mechanism

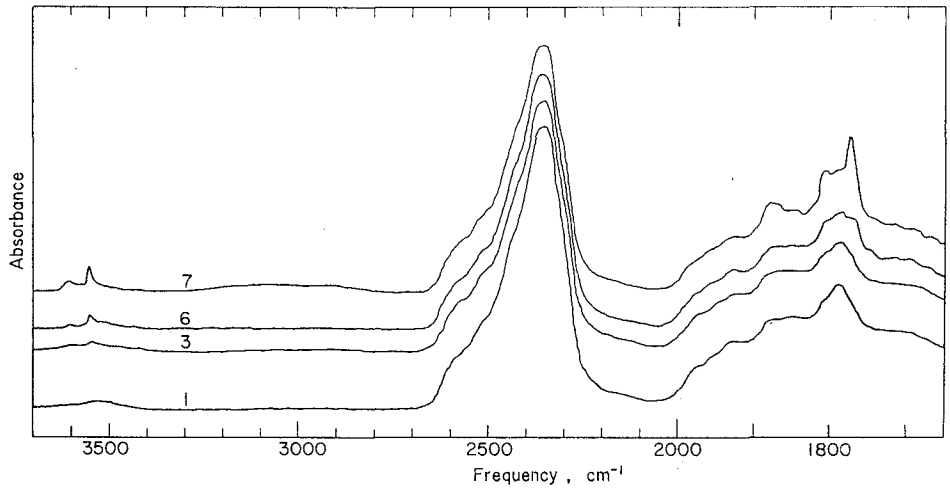

Fig. 5. Comparison of infrared spectra for samples, 1, 3, 6 and 7.

Table 2. Variation of dielectric loss maxima with γ-irradiation in the γ and δ relaxations of the copolymers with 11.9 mole % HFP.

Sample no.	Heat treatment for annealing[a]	Loss Maximum, $\varepsilon''_{max}\times10^4$	
		γ	δ
1	no	13.17	7.93
2	yes	12.60	7.60
3	no	13.92	7.84
4	yes	13.32	9.45
5	no	14.26	8.22
6	yes	14.10	10.33
7	no	15.54	8.75

[a] See text.

of the δ relaxation is not so straightforward as in the γ relaxation : the magnitude of the loss peak increased not only with irradiation but also with the heat treatment for annealing. It is likely that the relaxation is associated with polar groups rather than with degree of crystallinity in the copolymer. Eby and Wilson[3] suggested that the end CF_2H group would be responsible for this relaxation at low temperature, since all of the carboxylate end groups present in polymerization process of this particular copolymer are transformed to the CF_2H groups[7]. In this connection the variation of infrared absorption spectra in the 3700~1650 cm^{-1} region with γ-irradiation is shown for some samples in Fig. 7. The original copolymer sample shows a distinct band at 2350 cm^{-1} and a medium band at 1785 cm^{-1} which are observed as the combination bands in polytetrafluoroethylene[8]. These bands was not affected by the irradiation. A condiserable change in the spectra occurred at 3610, 3550, 1805 and 1770 cm^{-1} with an irradiation dose of about 3 MR. The absorption bands appeared at these frequencies by the irradiation can be assigned to the carboxylic group : the 3610 and 3550 cm^{-1} bands are attributed to the OH group and the 1805 and 1770 cm^{-1} bands to the CO group[9]. No absorption band expected for the CH vibration in the CF_2H group was found in the 3000 cm^{-1} region. From the results of infrared spectra it was considered that the size of the δ loss peak increased by the heat treatment for annealing would be related to the formation of the carboxylic groups.

Plots of the logarithm of the relaxation frequency versus the reciprocal of absolute temperature are shown for the γ and δ relaxations in Fig. 6. The activation enthalpy and entropy evaluated for two rexalations are listed in Table 3*. Values of the activation enthalpy and entropy for the γ relaxation increased gradually with higher irradiation doses. This is well understood in terms of the interaction between short segments increased in number by the chain scission and some contribution from polar groups produced by the irradiation. In the δ

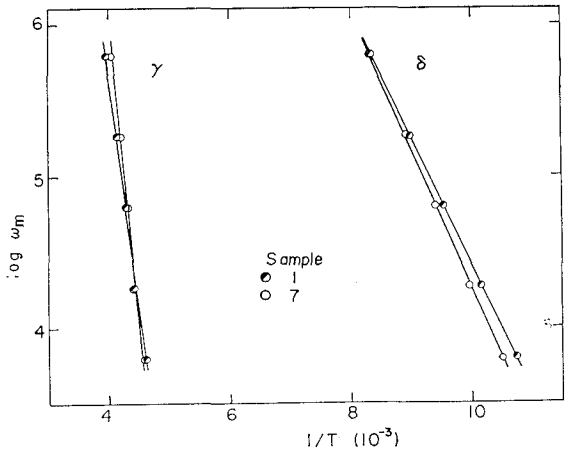

Fig. 6. Plots of logarithm of the relaxation frequency versus reciprocal of absolute temperature for the γ and δ relaxations.

* Values of ΔH and ΔS for the γ relaxation in this work are slightly greater than those reported previously which were evaluated from data in the limited temperature range[1,4].

Table 3. Activation parameters for the γ and δ relaxations in irradiated TFE-HFP copolymers.

Sample no.	Total irradiation dose, MR	γ relaxation		δ relaxation	
		ΔH, kcal/mole	ΔS, eu	ΔH, kcal/mole	ΔS, eu
1	0	14.3	25.4	3.4	0
2	0	15.0	27.9	3.5	0
3	1	14.8	32.7	3.5	0
4	1	16.0	32.2	3.5	0
5	3	17.5	39.3	3.7	0
6	3	17.6	38.8	3.6	0
7	10	17.5	38.2	3.7	0

relaxation almost no change in the activation parameters was found with the irradiation and the entropy with all of the samples was equal to zero. These facts suggest that the size of the molecular chain or groups involved in the δ relaxation would be quite small and possibly of the order of end groups. Whereas the polar groups produced by the irradiation contribute to the magnitude of loss peak, they would have little effect on the activation parameter, because these groups are still small in number and well separated with one other by the nonpolar perfluorocarbon chain.

CONCLUSION

It was confirmed that the γ dielectric relaxation at about 230°K in TFE-HFP copolymers is related to the molecular motion of short segments in amorphous regions. In addition to the γ relaxation the copolymer exhibited the δ relaxation, being much smaller in size, near 110°K which would be associated with the end groups. The size of the γ and δ loss peaks were influenced considrably by γ-irradiation. This effect was understood in terms of some contribution from the carboxylic groups possibly at the ends of moleuclar chain which were detected with infrared absorption spectra.

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